

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-012314

(43)Date of publication of application : 14.01.2000

(51)Int.Cl.

H01F 1/00

B01J 21/08

B03C 1/00

C01B 33/12

C01B 33/18

(21)Application number : 10-178627

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(22)Date of filing : 25.06.1998

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(54) LARGE BORE MAGNETIC SILICA PARTICLE AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a magnetic silica particle of large bore, together with a method for easily manufacturing it, which is useful as an adsorbent, adsorbing carrier, extractor-agent, extracting carrier, and catalyser carrier, etc., with small specific surface area, sufficient small bore volume, and large small bore.

SOLUTION: Si alkoxide and magnetic silica particle of large bore wherein, the content of magnetic material is 5-50 wt.% of the entire amount, average particle size of the silica particle is 1-200  $\mu\text{m}$ , BET specific surface area is less than 100  $\text{m}^2/\text{g}$ , small bore is 10 nm or less, and small bore volume is 0.3-2.5  $\text{ml/g}$ , are allowed to generate Si alkoxide polymer, which is allowed to carry magnetic material.

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's

decision of rejection]

[Date of requesting appeal against  
examiner's decision of rejection]

[Date of extinction of right]

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JAPANESE

[JP,2000-012314,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

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[Translation done.]

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## CLAIMS

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### [Claim(s)]

[Claim 1] The magnetic silica particle of the diameter of an osculum characterized by for the content of said magnetic substance being 5 - 50% of the weight of the whole quantity, for the mean particle diameter of said silica particle being 1-200 micrometers in the silica particle containing the magnetic substance, for a BET specific surface area being under 100m<sup>2</sup>/g, and for pore size being 10nm or more, and pore volume being 0.3 - 2.5 ml/g.

[Claim 2] The magnetic silica particle of the diameter of an osculum according to claim 1 characterized by a magnetic silica particle being spherical.

[Claim 3] The magnetic silica particle of the diameter of an osculum according to claim 1 or 2 characterized by the magnetic substance having superparamagnetism structure.

[Claim 4] In manufacturing the magnetic silica particle of the diameter of an osculum, a) Si alkoxide is hydrolyzed from an acid. The process which obtains the solution which is made to generate Si alkoxide polymer and contains Si alkoxide polymer at least, b) The magnetic substance is added to the solution which is obtained at the process of a and which contains Si alkoxide polymer at least. Contact in water the mixture obtained at the process and the process of c) of obtaining the mixture containing Si alkoxide polymer and the magnetic substance, and it spheroidizes. After washing the gel obtained at the process which adds and gels an alkali after that, and the process of d), The manufacture approach of the magnetic silica particle of the diameter of an osculum according to claim 1 to 3 which carries out the solvent permutation of the gel obtained at the process which carries out hydrothermal processing, and the process of e), pressurizing under heating, and is characterized by passing through five processes of process \*\* which is dried after that and obtains a magnetic silica particle at least.

[Claim 5] The manufacture approach of the magnetic silica particle characterized by calcinating further in the process e of the manufacture approach of a magnetic silica particle according to claim 4 after drying gel.

[Claim 6] The manufacture approach of the magnetic silica particle of the diameter of an osculum that viscosity of Si alkoxide polymer is characterized by being 10 - 1000 mPa·s in 25 degrees C in the process a of the manufacture approach of the magnetic silica particle of the diameter of an osculum according to claim 4 or 5.

[Claim 7] The manufacture approach of the magnetic silica particle of the diameter of an osculum characterized by using a magnetic fluid as a raw material of the magnetic substance in the process b of the manufacture approach of the magnetic silica particle of the diameter of an osculum according to claim 4 to 6.

[Claim 8] The manufacture approach of the magnetic silica particle of the diameter of an osculum characterized by carrying out hydrothermal processing in an autoclave with 110-380 degrees C and 1.4 to 220 atmospheric pressure in the process d of the manufacture approach of the magnetic silica particle of the diameter of an osculum according to claim 4 to 7.

[Claim 9] The manufacture approach of the magnetic silica particle of the diameter of an osculum that it is characterized by removing in the process e of the manufacture approach of the magnetic silica particle of the diameter of an osculum according to claim 4 to 8 after the processing permutes the moisture in gel with the organic solvent of low surface tension from water.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the magnetic silica particle and its manufacture approach of the diameter of an osculum which has the magnetism and reinforcement which can be used for an adsorbent, the support for adsorption, extractant and the support for an extract, catalyst support, etc.

[0002]

[Description of the Prior Art] the case where these are used although silica gel etc. is well known as an adsorbent or solid phase support for adsorption from before -- the recovery sake -- a centrifuge method -- or filtration with a filter etc. had to be performed and it was not a simple approach.

Moreover, in adsorption and extract operation, although the adsorbate and extract which are made into the purpose, and other other matter needed to be separated, by technique, such as the conventional centrifuge method, a column separation method, and an electrophoresis method, only separation required long duration and it had the technical problem that it was not a simple approach.

[0003] Therefore, there was a method of collecting the target particles by adding a ferromagnetic to a particle and giving a magnetic field like the publication to JP,61-181967,A as a means to separate the target matter. However, by this approach, in adsorption, an extract, reaction actuation, etc., the ferromagnetic itself carried out the self-association and it had the fault that a particle's existence condition was freely uncontrollable to carry out that actuation, after the particle has distributed to homogeneity.

[0004] In recent years, the approach using the superparamagnetism object as the magnetic substance is indicated like the publication to aforementioned JP,61-181967,A as an approach of losing the own self-association of a ferromagnetic. Moreover, it is indicated like the publication to \*\*\*\*\* 4-501957 using the magnetic particle which included the superparamagnetism object as solid phase which fixes a specimen that it can use for separation of protein, a cell, and DNA, analysis, etc. Furthermore, a gel matrix is made to catch the superparamagnetism MAG active substance to a patent number No. 2554250, and it is indicating about motile high reagent support to it. The superparamagnetism MAG particle given in these made ferromagnetics, such as an iron oxide, the particle smaller than the magnitude of a magnetic domain required to maintain permanent magnetism, and was made to contain them in a particle, and it has the property which shows ferromagnetism by the external magnetic field. The property is used, when making it distribute, an external magnetic field is not applied, but when making it condense, it is the approach of applying an external magnetic field and making the particle in a solution condensing. However, also in these approaches, it could not be said as what was obtained by the approach which fully controlled the physical properties of a magnetic particle, but the physical properties were fully controlled for the magnetic particle according to various applications, and a method of manufacturing the optimal magnetic particle was desired.

[0005] Moreover, it is shown that the silica particle which contains in JP,9-19292,A like a publication the superparamagnetism metallic oxide whose specific surface area is 100-800m<sup>2</sup>/g can use as an object for nucleic-acid association. However, although, as for the silica particle with a big specific surface area, the effectiveness of the specific surface area is expected to adsorption and association of the molecule of low molecular weight, since, as for the case of a molecule of the amount of macromolecules like a nucleic acid, association with a silica particle and a nucleic acid

almost takes place on a particle front face, neither specific surface area nor the effectiveness of pore structure is as remarkable as the matter of low molecular weight. Moreover, problems, such as adsorption of the impurity of low molecular weight and survival of the matter for washing, arise, and especially the increment in specific surface area, pore size, and pore volume generates problems, such as decline in washing effectiveness.

[0006] When especially aimed at macromolecules, such as a nucleic acid, it is thought that it results in being making specific surface area small and lessening pore, using the front face of silica gel alternatively, and raising the precision of adsorption or an extract, but when using only the front face of silica gel, reactive sites decrease in number and the effectiveness of a reaction is not high. Therefore, by losing small pore and leaving big pore, it is making it a reaction occur not only the front face of silica gel but within pore, and to make a reactive site increase and to raise reaction effectiveness is desired. Moreover, it is expected by losing small pore that adsorption of the impurity of low molecular weight and decline in washing effectiveness can be controlled.

[0007]

[Problem(s) to be Solved by the Invention] In view of a background, a technical problem, etc. which were indicated above, a specific surface area useful as an adsorbent, the support for adsorption, extractant and the support for an extract, catalyst support, etc. of the purpose of this invention is small, and it offers how it has sufficient pore volume and pore size can manufacture easily a silica particle with the magnetism of the big diameter of an osculum, and the magnetic silica particle of such a diameter of an osculum.

[0008]

[Means for Solving the Problem] In case the magnetic silica particle to which this invention persons included the magnetic substance of a constant rate in the raw material for forming a silica particle as a result of repeating examination wholeheartedly, in order to solve the above-mentioned technical problem, gel was made to form in, and magnetism was given is manufactured By manufacturing paying attention to physical properties, such as configurations, such as mean particle diameter of gel, a BET specific surface area, pore size, and pore volume, particle size, and a pore property A magnetic silica particle useful as the various support for adsorption, the support for an extract, and catalyst support is obtained, i.e., by contacting Si alkoxide polymer and the magnetic substance, spheroidizing, making it gel after that, and performing washing, hydrothermal processing, desiccation, and baking processing While being able to manufacture easily a magnetic silica particle with the suitable physical properties for various support, and leaving the pore of the big path in a magnetic silica particle especially by hydrothermal processing or enlarging further It finds out that the pore of a small path can be contracted or extinguished, and came to complete this invention.

[0009] That is, this invention relates to the magnetic silica particle and its manufacture approach of the diameter of an osculum characterized by for the content of said magnetic substance being 5 - 50% of the weight of the whole quantity, for the mean particle diameter of said silica particle being 1-200 micrometers, for a BET specific surface area being under 100m<sup>2</sup>/g, and for pore size being 10nm or more, and pore volume being 0.3 - 2.5 ml/g in the silica particle containing the magnetic substance.

[0010] Hereafter, this invention is explained to a detail.

[0011] First, the magnetic silica particle of this invention is explained.

[0012] Especially if it is the matter in which a magnetic property is shown as the magnetic substance used in the magnetic silica particle of this invention, it is not restricted, but when strong magnetism is generated by the ability of magnetism to be given and magnetism is lost, the lost thing which shows the so-called superparamagnetism is desirable. As what shows such a property, the alloy which used the ferrite of a spinel mold or a plan cutting tool mold, iron, nickel, cobalt, etc. as the principal component is mentioned, for example. The magnetic fluid which water and an organic solvent are made to suspend the ultrafine particle of magnetite or a ferrite, and is obtained also in these is used preferably, and this magnetic fluid is a fluid of colloid with which that diameter made magnetic particles, such as magnetite about 10nm or less and a ferrite, suspend in water or an organic solvent.

[0013] As a content of the magnetic substance in a magnetic silica particle, it is desirable that it is 5 - 50% of the weight of the magnetic silica particle whole quantity and further 5 - 25% of the weight of

the range. If it is this range, in a next door and an application side, it is easy for the magnetism of the magnetic silica particle obtained enough to make the front face of reaction effectiveness and the magnetic silica particle which separation actuation does not pose a problem and is obtained embellish chemically. Furthermore, also in a manufacture side, it is avoidable that can spheroidize, condensation of the magnetic substance becomes strong and the magnetic substance stops distributing the configuration of a magnetic silica particle to homogeneity inside a silica particle.

[0014] As range of the mean particle diameter of the magnetic silica particle of this invention, it is desirable that it is 1-200 micrometers. Gel is destroyed in a use side actual [ when mean particle diameter is less than 1 micrometer, a particle is too small, and ] when the rate of flow desirable in case time amount is taken too much in the case of separation or it uses in the fixed bed as support for catalysts may not no longer be acquired and it exceeds 200 micrometers, and it may be able to stop being able to maintain the configuration.

[0015] In order for the rate to the area on the front face of a particle of the area in particle pore to become low as range of the BET specific surface area of the magnetic silica particle of this invention, and for a solvent, the impurity of low molecular weight, etc. to stop being able to remain in a particle easily in an application side and to raise the precision of actuation, such as adsorption and an extract, and the processing time, under 100m<sup>2</sup>/g is desirable.

[0016] The pore structure of the magnetic silica particle of this invention can be measured as pore volume distribution with a method of mercury penetration using a pore sizer etc., as shown by the example. Here, as pore structure, although pore size and pore volume are called for, as pore size of the magnetic silica particle of this invention, it is determined in consideration of the magnitude of the measurement limitation of the measuring device used, and the particle of the measuring object.

[0017] in order to avoid that uptake of the impurity of low molecular weight etc. be carry out into pore, and it remain in a particle further since the pore size in the pore volume distribution of the fixed range measure as a pore size be mean and not only the front face of a magnetic silica particle but the interior of pore also use the matter of the amounts of macromolecules, such as a nucleic acid, as a part of adsorption or a reaction in an application side, it be desirable in this specification that it be 10 nm or more. Moreover, although it is required to be extent the reinforcement of a particle falls and it becomes impossible to attain the purpose of this invention as an upper limit of pore size, a clearance when the clearance between particles, for example, a 5-micrometer spherical particle, carries out the closest packing on the occasion of measurement of pore size is set to about 750nm. Although it is difficult to set clearly since it is hard coming to attach distinction with this clearance and the pore size of a particle, what is necessary is just usually a particle with pore size about 1500nm or less.

[0018] Moreover, in order that the matter of the amounts of macromolecules, such as a nucleic acid, may also use [ in / it is desirable that the pore mode diameter to which frequency becomes high most in pore volume distribution is also large, and / an application side ] not only the front face of a magnetic silica particle but the interior of pore as a part of adsorption or a reaction, In order for 10nm or more to make it further easy much more to enter the interior of pore in the matter of the amount of macromolecules in order to avoid that uptake of the impurity of low molecular weight etc. is carried out into pore, and it furthermore remains in a particle and to enable it to use, a certain thing is desirable 25nm or more.

[0019] As range of the pore volume of the magnetic silica particle of this invention, it is still more desirable that it is 0.3 - 2.5 ml/g. When a reactive site may decrease, reaction effectiveness may fall, when pore volume is less than 0.3 ml/g, and pore volume is larger than 2.5 ml/g, the reinforcement of gel may fall and it may destroy while in use. Furthermore, if this range is 0.5 - 2.0 ml/g, it is much more desirable in respect of reaction effectiveness and the reinforcement of gel.

[0020] Next, the manufacture approach of the magnetic silica particle of this invention is explained.

[0021] Although it is desirable as a start raw material of the magnetic substance in the magnetic silica particle of this invention that it is a magnetic fluid and the manufacture approach can be enforced by the well-known approach, it can manufacture still more easily by the manufacture approach which consists of the following processes.

[0022] a) Hydrolyze Si alkoxide from an acid and make Si alkoxide polymer generate. The magnetic substance is added to the solution which is obtained at the process and the process of ba of obtaining



the solution which contains Si alkoxide polymer at least and which contains Si alkoxide polymer at least. Contact in water the mixture obtained at the process and the process of cb of obtaining the mixture containing Si alkoxide polymer and the magnetic substance, and it spheroidizes. The process which carries out the solvent permutation of the gel obtained at the process which carries out hydrothermal processing, and the process of ed after washing the gel obtained at the process which adds and gels an alkali after that, and the process of dc, pressurizing under heating, is dried after that, and obtains a magnetic silica particle.

[0023] Process a

As an Si alkoxide used in the manufacture approach of this invention In the manufacture approach shown below, if hydrolysis generates a polymer, it can use without a limit especially. For example, Si (OCH<sub>3</sub>)<sub>4</sub>, Si (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, Si (O-n-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, Si (O-i-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, Si (O-n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, and Si(O-i-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> grade can be mentioned. Moreover, in the manufacture approach of this invention, other metal alkoxides, such as Ti, Zr, and aluminum, may be added in addition to Si alkoxide.

[0024] It hydrolyzes partially to extent which does not gel the alkoxide of Si in an acidic solution probably. As an acidic solution, the mixed solution of an acid, water, and an organic solvent is desirable. As an acid used at this time, organic acids, such as inorganic acids, such as a hydrochloric acid, a sulfuric acid, and a nitric acid, an acetic acid, and a formic acid, are mentioned. What is mixed with an acid, water, and Si alkoxide to homogeneity as an organic solvent is desirable, and alcohol, such as a methanol and ethanol, is especially desirable. As for the amount of the water to add, it is desirable that it is less than four mols to one mol of amounts which hydrolyze Si alkoxide partially, i.e., Si alkoxide. As conditions for a hydrolysis reaction, in order to make Si alkoxide hydrolyze to homogeneity, it is good by being the range of 10-80-degree C temperature, and making a mixed solution agitate for 30 minutes to 5 hours.

[0025] After hydrolyzing Si alkoxide, the polymerization of the above-mentioned Si alkoxide solution is carried out next. As polymerization conditions, it is possible to carry out in the range with a temperature of 10-200 degrees C for 1 to 48 hours, after a reaction, the alcohol generated at the solvent or the reaction is removed, and Si alkoxide polymer is obtained. The polymerization degree of Si alkoxide polymer, i.e., molecular weight, is controllable by the amount of water, polymerization temperature, polymerization time amount, etc.

[0026] Correlation is between the polymerization degree of Si alkoxide polymer, and viscosity, and viscosity becomes high, so that the polymerization degree of Si alkoxide polymer becomes high. It is desirable that it is extent to which gelation does not take place as polymerization degree of Si alkoxide polymer, and they are the range of 10 - 1000 mPa-s and the range of further 20 - 500 mPa-s in the viscosity in a room temperature. When viscosity is less than 10 mPa-s, in case the magnetic substance may become in the next process b that it is hard to distribute Si alkoxide polymer to homogeneity when viscosity exceeds 1000 mPa-s, and this reason is made to gel in the next process c, it is because gelation may stop being able to happen easily. Moreover, viscosity here can be checked by measuring the viscosity in 25 degrees C based on JIS-K -7117-1987.

[0027] Obtained Si alkoxide polymer prepares the solution diluted and mixed with remaining as it is or an organic solvent, and uses it as the solution which contains Si alkoxide polymer at least. When diluting Si alkoxide polymer with an organic solvent, as an organic solvent used, what it is hard to dissolve in water, such as alcohol, such as hydrocarbons, such as a hexane, a cyclohexane, and benzene; 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 1-hexanol, and 2-hexanol, is desirable. In case this reason manufactures a magnetic silica particle, it is for spheroidizing by distributing the phase containing Si alkoxide polymer in water. Moreover, it is desirable that it is 20 % of the weight or more to the solution whole quantity diluted in order to obtain spherical gel as concentration of Si alkoxide polymer in the case of diluting with an organic solvent.

[0028] Process b

Next, the magnetic substance is added to the solution which is obtained at Process a and which contains Si alkoxide polymer at least, and the mixture containing Si alkoxide polymer and the magnetic substance is obtained. As the magnetic substance used, what what water or an organic solvent was made to distribute and was made into the shape of the shape of suspension and a solution was desirable, and contained the organic solvent as a dispersant further is preferably used from the field of the dispersibility to Si alkoxide polymer, it has the small particle diameter which is

especially about 10nm, and a magnetic fluid with the sufficient dispersibility and its stability to Si alkoxide polymer of this magnetic particle is used preferably. As this magnetic fluid, remaining as it is or a solvent permutation can be carried out, and a commercial item etc. can also be used.

[0029] Here, in distributing the magnetic substance to a polymer, it is desirable to make a mixed solution with Si alkoxide polymer or its diluent solvent distribute the magnetic substance to homogeneity.

[0030] On the occasion of the addition to Si alkoxide polymer of the magnetic substance, the magnetic substance of the specified quantity can also be added directly and the solution which made the solvent distribute the magnetic substance beforehand can also be added to Si alkoxide polymer.

[0031] Moreover, as a solvent, in case the solution which made the solvent distribute the magnetic substance is prepared, in order to secure the dispersibility of the magnetic substance to Si alkoxide polymer, it is desirable to use a polar low organic solvent. As an example of such an organic solvent, alcohol, such as hydrocarbons, such as a hexane, a cyclohexane, and benzene, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 1-hexanol, and 2-hexanol, etc. is mentioned. Furthermore, the alcohol of 4-6 is preferably used [ these Uchi ] for a carbon number. Although this reason contacts the mixture containing Si alkoxide polymer and the magnetic substance in water and spheroidizes as a suspension condition at the following process c, it is because it is suitable for the solubility to water maintaining such a suspension condition, and making the reaction of subsequent gelation perform promptly in that case.

[0032] Furthermore, in order to distribute the magnetic substance in the magnetic substance mixed with the solvent, or a magnetic fluid, to lose condensation of the magnetic substance and to stabilize a distributed condition, it is desirable to process a front face and near a front face the magnetic substance with a surfactant etc., or to add a surfactant. Moreover, in case the magnetic substance is mixed with Si alkoxide polymer, in order to make homogeneity distribute the magnetic substance, as polymerization degree of Si alkoxide polymer, what is necessary is just the range of the above mentioned viscosity. It is because the molecular weight of Si alkoxide polymer contributes also to the dispersibility of the magnetic substance, and its stability, and does not become viscosity, either, so actuation will become easy if it is this range.

[0033] Thus, the mixture which homogeneity is made to distribute the magnetic substance to Si alkoxide polymer, and contains Si alkoxide polymer and the magnetic substance can be obtained by combining the class of magnetic substance, the polymerization degree of Si alkoxide polymer, and the diluent solvent of Si alkoxide polymer.

[0034] Process c

Next, it is made to distribute underwater under churning, the mixture containing Si alkoxide polymer and the magnetic substance which were obtained at Process b is suspended, and it spheroidizes. Here, in order to improve the dispersibility of the magnetic substance further, dispersants, such as a surface active agent and polyvinyl alcohol, may be added to the water used.

[0035] An alkali is added and gelled to the mixed liquor or mixture of the above-mentioned publication after balling-up. Although the detailed device of gelation is not clear, it is thought that it gels because the alkoxide radical in Si alkoxide polymer hydrolyzes according to an operation of an alkali, a silanol group generates, this silanol group joins together in three dimensions by the condensation reaction and the polymer of a silica generates. As an alkali used, organic base nature compounds, such as inorganic base nature compounds, such as ammonia, a sodium hydroxide, and a potassium hydroxide, an amine, and a urea, are mentioned. In order to hydrolyze the alkoxy group in Si alkoxide polymer nearly completely in the case of gelation, it is good by agitating in the pH range of pH 8-11, and a 30-100-degree C temperature requirement for 1 to 10 hours.

[0036] Process d

Filtration, centrifugal separation, etc. separate and the generated gel which was obtained at Process c is washed. An approach well-known as the approach of filtration and separation can be used, and the water usually used, such as water and warm water, can be used for washing.

[0037] Subsequently, hydrothermal processing is carried out, pressurizing under heating of the washed magnetic silica gel.

[0038] What is necessary is just equipment which can give the conditions of pressurization and heating, preparing a solution like an autoclave as equipment used for this hydrothermal processing.

And magnetic silica gel is taught to an autoclave, an alkali water solution like water or aqueous ammonia is added, predetermined temperature and the conditions of a pressure are set up, and hydrothermal processing is carried out.

[0039] As conditions for hydrothermal processing, it is desirable to carry out by the pressure of the temperature of 110-380 degrees C and 1.4 to 220 atmospheric pressure, and it is still more desirable to carry out by the pressure of the temperature of 150-250 degrees C and four to 40 atmospheric pressure. As effectiveness of hydrothermal processing, if it is in this range, although the specific surface area of the magnetic silica gel obtained becomes small, it will become large as that average pore size, and will become very useful in a reaction effectiveness side. On the other hand, hydrothermal conditions may become inadequate in the case of less than 110 degrees C, pore size may not become large, and equipment becomes large-scale at temperature which exceeds 380 degrees C, and temperature control is well impossible or it is not sometimes economical. Moreover, as time amount of hydrothermal processing, although it is not fixed with the conditions of temperature and a pressure, it is usually enough in about 1 - 24 hours.

[0040] Process e

Furthermore, the solvent permutation of the gel obtained at Process d is carried out, and it dries.

[0041] If the moisture on the interior of gel and the front face of gel is evaporated directly, since gel will contract and condense as desiccation conditions, it is good to dry by the following approaches.

[0042] That is, after an organic solvent permutes the moisture in the washed gel, gel is dried by carrying out heating etc. and removing an organic solvent. In order to prevent gels condensing the permutation processing by this organic solvent strongly according to the capillary force produced in case the water which exists in the interior of gel evaporates, it is for permuting by the organic solvent with low surface tension beforehand, weakening capillary force, and making desiccation of gel easy.

As an organic solvent used for this permutation processing, the solvent of low surface tension is more desirable than water, and what melts together at a rate of water and arbitration is still more desirable. the solvent of the low surface tension [ water ] in here -- Wilhelm of water -- since the surface tension to the air in 25 degrees C by law is 72 dyn/cm (= 10Nm), the solvent which has surface tension smaller than this can be chosen. For example, alcohol, such as a methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol, a formamide, N.N-dimethylformamide, ethylene glycol, propylene glycol, etc. are mentioned as a solvent.

[0043] Although removal of the water which remains in the gel after an organic solvent permutes, and a solvent is performed by heating in ordinary pressure, only reduced pressure can be decompressed under heating and it can also usually perform it. Moreover, when condensation of gel is strong, after distributing water and an organic solvent again, it permutes by the organic solvent, heating removal is carried out after that, and you may make it gel not condense.

[0044] Moreover, a magnetic silica particle can also be dried by removing the water in gel with the solvent which added, heated and used the organic solvent. As an organic solvent used here, a high-boiling point and the solvent of low surface tension are more desirable than water, and ketones, such as ester, such as alcohol, such as 1-butanol, isobutyl alcohol, 1-pentanol, 2-pentanol, 3-pentanol, and isoamyl alcohol, methyl butyrate, and ethyl butylate, cyclopentanone, 3-heptanone, and 4-heptanone, etc. are mentioned. Although removal of water and a solvent is performed by ordinary pressure, it may usually be performed under reduced pressure.

[0045] Furthermore, you may calcinate in order to raise the reinforcement of the desiccation silica gel obtained at Process e. As baking conditions, a magnetic silica particle can be obtained among an atmospheric-air ambient atmosphere by calcinating in an inert atmosphere like nitrogen gas, or reducing atmosphere like hydrogen gas. In order that the pore structure of the magnetic silica particle obtained may hold as temperature conditions in the case of baking, 1000 degrees C or less are desirable. If burning temperature exceeds 1000 degrees C, contraction of a magnetic silica particle arises, pore size becomes small, and the particle of the diameter of an osculum may not no longer be obtained.

[0046] Moreover, when carrying out chemical modification of the front face of the obtained magnetic silica particle, the specific surface area of a magnetic silica particle is small, and a silica particle is contacted to a hydrofluoric acid etc., and when there is little abundance of a silanol group, beforehand, the surface amount of silanol groups can adjust to a front face, and it can be used for it.

[0047] The magnetic silica particle of this invention is obtained by the above technique.

[0048] Moreover, mainly the magnetic silica particle of this invention can be used as it is as adsorption, an extract, and an object for a reaction using a hydrophilic interaction, a hydrophobic radical can be introduced, and it can also carry out [ a silanol group exists in the front face, ] chemical modification of the front face of a magnetic silica particle, and can use it also for the application using a hydrophobic interaction.

[0049] Furthermore, it can be made to be able to combine with protein, such as an antibody and an enzyme, a peptide, a nucleic acid, etc. which are a living thing origin ingredient, and can also be used as immobilization support used for separation means, such as various kinds of measuring methods, such as immunoassay and measurement of a nucleic acid, and affinity chromatography, etc. Moreover, it can also be used as a magnetic material or a spacer.

[0050] Although the magnetic silica particle of this invention has large pore size and the specific surface area is small, dissolve and the silica in gel re-deposits because this performs hydrothermal processing to the obtained magnetic silica particle. Most small things of the path in pore are lost, however the big thing of the path in pore is considered [ maintenance or ] to become large rather in the path. As the result The matrix of a silica becomes strong, and while it is expectable that compressive strength, abrasion resistance, and shock resistance improve, the ratio of the pore of a big path becomes large.

[0051] However, such a guess does not restrain this invention at all.

[0052]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited at all to these by the example. In addition, each evaluation was carried out by the approach shown below.

[0053] When the magnetic hysteresis was measured for the magnetic hysteresis about the magnetic fluid used in the example using the oscillating sample mold magnetometer (VSM) (the product made from the Riken electron, form: BHV-50), it was what shows superparamagnetism.

[0054] (1) About the content Si of the magnetic substance, perchloric acid processing was carried out after decomposition with the aqua regia, and the magnetic silica particle was measured with the weight method. About Fe (iron), perchloric acid processing was carried out after decomposition by the nitric acid and the hydrofluoric acid, and it measured by the ICP emitting-light method.

[0055] (2) A part of mean-particle-diameter magnetism silica particle was observed by scanning electron microscope ISI-130 (product made from COULTER), and it asked for it with the intercept method.

[0056] (3) It measured with the method of mercury penetration in the pressure range of 0-207MPa using the pore structure pore sizer 9320 (product made from MICROMERITICS). In addition, 6nm which is a measurement limitation was made into the measurement minimum as a result obtained, and 500nm was made into the measurement upper limit in order to avoid that the clearance between particles is reflected in measurement. And the pore mode diameter and pore volume which show pore size with the highest frequency the range of pore size and among distribution of pore size were measured.

[0057] (4) It measured by law one BET equation using BET specific surface area MONOSORB (product made from U.S. QUANTACHROME).

[0058] (5) Based on viscosity JIS-K-7118-1987, the viscosity in 25 degrees C was measured by the Brookfield viscometer (the Tokyo Keiki Co., Ltd. make, form: BH).

[0059] (6) It measured by the following approaches that the internal analysis magnetic substance of gel was distributed over the interior of a magnetic silica particle. That is, embedding of the magnetic silica particle was carried out with the epoxy resin, and the microtome cut. C (carbon) vacuum evaporation of the front face was carried out here the back, scanning electron microscope (SEM) observation of this was first carried out using JCMS-733 (JEOL Co., Ltd. make), the configuration of a magnetic silica particle was checked, and EPMA (Electron Probe Microanalysis) analyzed distribution of Si and Fe in a magnetic silica particle further.

[0060] Example 1Si<sub>4</sub>(OC<sub>2</sub>H<sub>5</sub>) 75.0g and ethanol The 30.0g mixed solution was agitated at 40 degrees C for 30 minutes. It is 1/100N-hydrochloric-acid water solution, agitating this mixed solution at 40 degrees C. 7.5g was dropped. After agitating this solution for 1 hour, it agitated at 165

more degrees C by 90 degrees C for 12 hours for 4 hours, the distillate was removed, and Si alkoxide polymer was obtained. This actuation was performed in nitrogen-gas-atmosphere mind. When measured by the approach which described above the viscosity of obtained Si alkoxide polymer, viscosity was 75 centipoises at the room temperature. It is 1-pentanol about 35.0g of obtained Si alkoxide polymer. It dissolved in 35.0g. Magnetic fluid of marketing in this solution (they are the 35 % of the weight of the amounts of magnetic substance, the 10 % of the weight of the amounts of surface active agents, and 1-butanol solution content to Ferrotec Make and :whole quantity) 10ml was added and the homogeneity solution was obtained. It is 80-degree C 5% polyvinyl alcohol water solution, agitating this solution. It supplied to 280.0g. After 30-minute churning, 5% of the weight of aqueous ammonia solution 12.5ml was added and it agitated at 80 degrees C for 3 hours. It is 70-degree C warm water about the obtained suspension. It supplied to 500ml and warm water washed after separating a solid-state. Hydrothermal processing was carried out for the magnetic silica particle to the basis of the pressure of ten atmospheric pressures at the temperature of 180 degrees C in the autoclave after washing for 4 hours. Next, by 2-propanol, it permuted 3 times, the vacuum drying was carried out, and the magnetic silica particle was obtained. It measured by the approach which described above Fe content of the obtained magnetic silica particle, a Si/Fe presentation (mole ratio), mean particle diameter, and a BET specific surface area, and the result was shown in Table 1. Moreover, it was spherical when observed by SEM which described the obtained magnetic silica particle above. Furthermore, by EPMA, when distribution of Si and Fe in a magnetic silica particle was analyzed, it checked that Fe, i.e., the magnetic substance, was distributing to homogeneity in a magnetic silica particle.

[0061]

[Table 1]

|      | Siアルコキシド<br>ポリマーの粘度<br>(mPa・s) | Fe含有量<br>(重量%) | Si/Fe組成<br>(モル比) | 平均粒径<br>( $\mu$ m) | BET比表面積<br>( $m^2/g$ ) | 細孔径範囲<br>(nm) | 細孔モード径<br>(nm) | 細孔容積<br>(ml/g) |
|------|--------------------------------|----------------|------------------|--------------------|------------------------|---------------|----------------|----------------|
| 実施例1 | 75                             | 14.5           | 4.7              | 5.9                | 90                     | 10~500        | 25             | 1.56           |
| 実施例2 | 68                             | 14.0           | 4.6              | 6.8                | 62                     | 10~500        | 40             | 1.58           |
| 比較例1 | 82                             | 14.3           | 4.7              | 4.9                | 356                    | 300以下         | 30             | 0.87           |
| 比較例2 | 70                             | 15.0           | 4.9              | 6.0                | 132                    | 300以下         | 10             | 1.44           |

[0062] Moreover, when pore volume distribution, pore volume, etc. were measured with the method of mercury penetration using the pore sizer 9320 which described the obtained magnetic silica particle above, as shown in Table 1, the pore mode diameter which the pore size range is set to 10-500nm (measurement upper limit), and shows the peak was 25nm, and pore volume was 1.56 ml/g.

[0063] By the same approach as example 2 example 1, the gel performed to rinsing processing was put into 1.5% of the weight of the aqueous ammonia solution, and hydrothermal processing was carried out to the basis of the pressure of 23 atmospheric pressures at the temperature of 220 degrees C in the autoclave for 4 hours. In addition, the viscosity of Si alkoxide polymer was 68 centipoises at the room temperature. Then, next, by 2-propanol, it permuted 3 times, the vacuum drying was carried out, and the magnetic silica particle was obtained. The obtained magnetic silica particle was measured by the same approach as an example 1, and the result was shown in Table 1. Moreover, it was spherical when observed by SEM which described the obtained magnetic silica particle above. Furthermore, by EPMA, when distribution of Si and Fe in a magnetic silica particle was analyzed, it checked that Fe, i.e., the magnetic substance, was distributing to homogeneity in a magnetic silica particle.

[0064] Moreover, when pore volume distribution, pore volume, etc. were measured like an example 1, as the obtained magnetic silica particle was shown in Table 1, the pore mode diameter which pore size is set to 10-500nm (measurement upper limit), and shows the peak was 40nm, and pore volume was 1.58 ml/g.

[0065] By the same approach as example of comparison 1 example 1, the gel which went to rinsing processing was used as it was, without carrying out hydrothermal processing, by 2-propanol, it permuted 3 times, the vacuum drying was carried out, and the spherical magnetic silica particle was obtained. In addition, the viscosity of Si alkoxide polymer was 82 centipoises at the room temperature. The obtained magnetic silica particle was measured by the same approach as an example 1, and the result was shown in Table 1.

[0066] Moreover, the obtained magnetic silica particle is shown in Table 1, when pore volume distribution, pore volume, etc. are measured like an example 1, Although the pore mode diameter which pore size is set to 300nm or less, and shows that peak was 30nm, the height of a peak is also low, and pore exists and the BET specific surface area of this particle can presume further even the 6nm neighborhood which is the minimum community value of this measurement to be that to which pore exists in 6nm or less below measurement threshold value also from a large thing with 356m<sup>2</sup>/g. Pore volume was still as smaller as 0.87 ml/g.

[0067] By the same approach as example of comparison 2 example 1, the gel performed to rinsing processing was put into 1.5% of the weight of the aqueous ammonia solution, and hydrothermal processing was carried out to the basis of the pressure of 1.2 atmospheric pressures at the temperature of 105 degrees C in the autoclave for 4 hours. In addition, the viscosity of Si alkoxide polymer was 70 centipoises at the room temperature. Then, next, by 2-propanol, it permuted 3 times, the vacuum drying was carried out, and the magnetic silica particle was obtained. The obtained magnetic silica particle was measured by the same approach as an example 1, and the result was shown in Table 1.

[0068] Moreover, the obtained magnetic silica particle is shown in Table 1, when pore volume distribution as well as an example 1 is measured, Although the pore mode diameter which pore size is set to 300nm or less, and shows that peak was 10nm, pore exists and the BET specific surface area of this particle can presume further even the 6nm neighborhood which is the minimum community value of this measurement to be that to which pore exists in 6nm or less below measurement threshold value also from a large thing with 132m<sup>2</sup>/g. Furthermore, pore volume was 1.44 ml/g.

[0069] When the result of examples 1 and 2 is compared with the result of the examples 1 and 2 of a comparison, it turns out that the pore size becomes large by performing moderate hydrothermal processing to a magnetic silica particle in spite of the configuration of a particle and particle size being almost changeless, and specific surface area becomes small further. This is supported from the pore mode diameter of the magnetic silica particle obtained by making high the conditions of the example 1 of a comparison which did not perform hydrothermal processing and hydrothermal temperature, and a hydrothermal pressure with the example 2 of a comparison, an example 1, an example 2, and steps being large. Furthermore, about pore volume, it turns out that it is large by performing hydrothermal processing.

[0070]

[Effect of the Invention] It is spherical, and the magnetic silica particle of this invention contains the magnetic substance of sufficient amount for the interior, and its pore volume is also fully large. and the pore size is large -- \*\*\*\* and specific surface area are comparatively small from being alike. Furthermore, since reconstruction of association of a silica occurs by hydrothermal processing, the matrix of a silica becomes strong, and it can be expected that compressive strength, abrasion resistance, and shock resistance will improve. For this reason, it can be suitably used as an adsorbent, the support for adsorption, extractant and the support for an extract, and catalyst support.

[0071] Moreover, according to the manufacture approach of this invention, specific surface area is small, and pore size is large and can manufacture easily a magnetic silica particle also with sufficiently large pore volume.

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[Translation done.]